Synthesis of a Vinyl Monomer Containing β-Cyclodextrin and Grafting onto Cotton Fiber

MYUNG HAK LEE,[1] KEE JONG YOON,[2] SOHK-WON KO[3]

[1] Korea Textile Inspection and Testing Institute (KOTITI), Seoul 135-081, South Korea

[2] School of Textile and Polymer Engineering, Dankook University, Seoul, 140-714, South Korea

[3] Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, South Korea

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ABSTRACT: To chemically bond β-cyclodextrin (β-CD), which can form inclusion complexes, acrylamidomethyl CD (CD–NMA) obtained from the acid-catalyzed reaction of *N*-methylolacrylamide (NMA) and β-CD was grafted onto cellulose fibers using CeIV as the initiator. The double-bond content of CD–NMA increased with increase in the NMA/CD mol ratio, and a CD–NMA containing a maximum of three molecules of NMA bonded to a CD molecule could be obtained. Since the grafting condition is acidic, the hydrolytic stability of CD–NMA in aqueous nitric acid was studied. The temperature of hydrolysis proved to have a greater effect on the depletion of double bonds from CD–NMA compared with the concentration of the acid. Thus, CD–NMA was grafted onto cellulose fibers at a low temperature, and FTIR analysis of the CD–NMA-grafted cotton fibers confirmed the chemical bonding of CD–NMA molecules to cellulose. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 438–446, 2001

Key words: β-cyclodextrin; *N*-methylolacrylamide; acrylamidomethyl cyclodextrin; cotton fiber; grafting

INTRODUCTION

Cyclodextrin (CD), first isolated in 1891 by Villiers and characterized as cyclic oligosaccharides in 1904 by Schardinger, can be obtained from degradation of starch with a glucosyltransferase enzyme. They are cyclic oligosaccharides consisting of six, seven, or eight glucose units which are joined together by $\alpha(1 \rightarrow 4)$ linkages.[1,2]

The oligosaccharide ring forms a torus with the primary hydroxyl groups of glucose residues lying on the narrow end of the torus, since the free rotation of the primary hydroxyls reduces the effective diameter of the cavity. The approximate dimensions of CD are shown schematically in Scheme 1.[3] The most important characteristic of CD may be the capability of forming inclusion compounds where the host component admits a guest component into its cavity without forming any covalent bonds. Since only a few guest molecules are entrapped by one, two, or three CD molecules compared with microencapsulation, where 10^{10} to 10^{13} guest molecules are entrapped, the inclusion process is often termed "molecular encapsulation."[4] The molecular encapsulation capability of CD is utilized in many fields such as foods, cosmetics, pharmaceuticals, analytical chemistry, and chromatography. About one-third of all patents and potential applications published before 1985 dealt with pharmaceutical applications.[5] For example, CDs can be used in drugs as inclusion complexes or as auxiliary ad-

Correspondence to: M. H. Lee.

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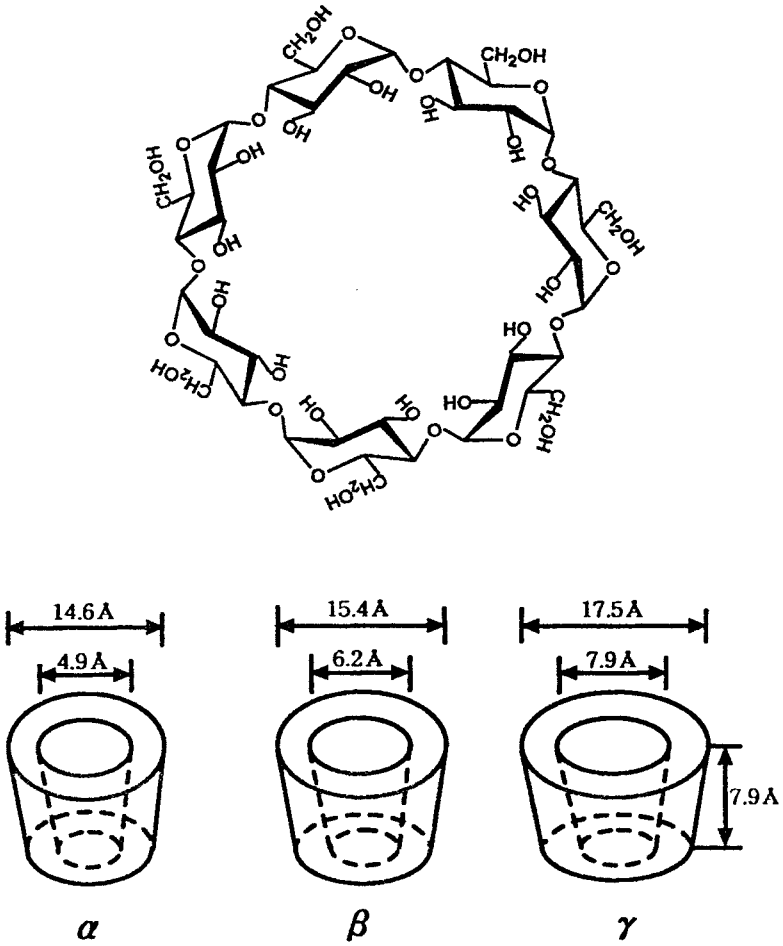

Scheme 1 Structure of β-CD and molecular dimensions of α, β, and γ-CD.

ditives. An inclusion complex formation of a drug results in the modification of its physical and chemical properties, which are usually advantageous in the formulation of oral drugs. For example, improvements in the physical and chemical stability and in the bioavailability of poorly soluble drugs may be obtained.

The potential advantages of utilization, the availability of CD, and economic factors has resulted in increased interest in the application of CD in textile finishing. Numerous patents and articles on the application of CD in insect-free and mite-repellent finish, antimicrobial finish, aroma finish, etc., have been reported since 1985. However, in these publications, CD was bound physically to the fibers using binders.

In this study, an attempt was made to chemically bond CD to cellulose instead of using binders to physically attach the CD molecules. CD was first reacted with *N*-methylolacrylamide (NMA) using an acid catalyst to prepare the acrylamidomethyl CD monomer. Optimum conditions for the acrylamidomethylation of CD were determined by varying the reaction conditions; then, the acrylamidomethyl CD monomer was grafted onto cellulose fibers.

EXPERIMENTAL

Materials and Reagents

Scoured and bleached cotton fibers were used. β-CD (Nihon Shokuhin Kako Co.) was recrystallized in water three times and dried at 110°C for about 4 h and kept in a desiccator. NMA (Tokyo Kasei Kogyo Co., extrapure grade), 35% hydrochloric acid (Junsei Chemical Co., Tokyo, extrapure grade), 85% formic acid (Junsei Chemical Co., extrapure grade), and ceric ammonium nitrate (CAN, Kanto Chemical Co., Tokyo, guaranteed grade) were used as received without further

purification. Other extrapure grade and guaranteed grade chemicals were also used as received and distilled deionized water was used.

Synthesis of Acrylamidomethyl CD-grafted Cellulose Fibers

Synthesis of Acrylamidomethyl CD (CD–NMA)

Purified CD, NMA, and an acid catalyst were added to 50 mL of water in a three-neck reactor equipped with a mechanical stirrer, thermometer, and condenser. NMA/CD mol ratios of 5, 10, 15, 20, and 30, reaction temperatures of 70, 80, and 90°C, reaction times of 5–60 min, and the type and amount of the catalyst, that is, hydrochloric acid, formic acid, or ammonium phosphate, were investigated to obtain the optimum reaction conditions. Upon completion of the reaction, 300 mL of acetone was added and the mixture stored at 5°C to allow complete precipitation of the products. The precipitates were filtered, washed several times in 200 mL acetone, dried at 30°C in a vacuum drying oven for 12 h, and then stored in a refrigerator.

Grafting

Grafting was carried out in a three-neck reactor equipped with a stirrer, condenser, and nitrogen inlet tube. Approximately 0.5 g of cotton fibers and a 0.012*M* CAN solution in 1% nitric acid were added to make a solids content of 1%. After stirring the mixture for 20 min with a nitrogen purge, 10 g of CD–NMA was added and reacted at 40 or 60°C for 1 h. On completion of the reaction, the product was washed sufficiently with running water to remove unreacted monomers and homopolymers, neutralized with 1% sodium carbonate, washed again with running water, then washed in boiling water for 30 min and dried at 110°C for 1 h. The graft yield was calculated from the initial weight of the cellulose and the measured weight of the product from which residual monomers and homopolymers had been removed by the above procedure.

Analysis

Double-bond Content

The double-bond content of CD–NMA was determined according to the method used by Kamel et al.[6] Approximately 1 g of CD–NMA was added to 10 mL of water in a glass bottle; then, 10 mL of 3% mercaptoethanol and 2 mL of 2 mol/L sodium hydroxide were added and stirred at room temperature for 60 min to carry out the addition of the mercaptoethanol to the double bonds. The amount of residual mercaptoethanol was determined by oxidative titration with a 0.1 mol/L iodine solution using a 0.5% starch solution as an indicator after adding 5 mL of 1 mol/L hydrochloric acid. The double-bond content was calculated using the following equation:

$$\text{Double-bond content (mmol/g CD–NMA)} = \frac{(V_B - V_S) \times 0.1 \times f}{W}$$

where W is the weight of the sample (g); V_B, the amount of the iodine solution used in the blank titration (mL); V_S, the amount of the iodine solution used in the sample titration (mL); and f, the factor of a 0.1 mol/L iodine solution.

Infrared Analysis

The samples were made into KBr pellets and scanned 64 times on a Magna-IR 550 (Nicolet) FTIR spectrometer at a resolution of 4 cm^{-1}.

HPLC Analysis

To confirm the absence of residual unreacted NMA in CD–NMA, the CD–NMA product was separated using an LC-10AD HPLC (Shimadzu, Japan) equipped with a Sugar-Pak column (size 6.5 × 300 mm) at 90°C using water at 0.5 mL/min as the eluent.

Acid Hydrolysis Susceptibility of CD–NMA

The susceptibility of CD–NMA toward acid hydrolysis was evaluated by measuring the residual double-bond content after hydrolysis in a nitric acid solution. The residual double-bond contents of approximately 5-mL aliquots taken from the solution at fixed intervals were determined. The CD and CD–NMA in the aliquots were precipitated with about 50 mL of acetone, filtered, washed with fresh acetone, and vacuum-dried at room temperature prior to analysis.

RESULTS AND DISCUSSION

CD has generally been reacted with bi- or multifunctional compounds capable of reacting with hydroxy groups in the preparation of CD poly-

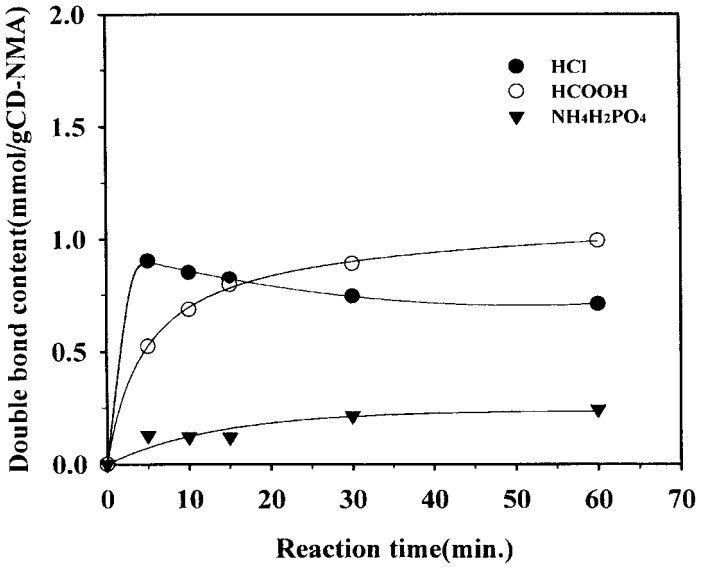

Figure 1 Influence of catalysts and reaction time on the double-bond content in CD–NMA. Reaction conditions: CD, 15 g; CD : NMA, 1 : 10; water, 50 mL; temperature, 80°C; catalyst concentration, 1%.

mers. The bifunctional compounds typically employed for this purpose, diisocyanates or diepoxides, have limited solubility and react with water. Thus, these bifunctional compounds could not be used in conventional textile-finishing processes which employ water as the medium, and research on the chemical bonding of CD via a typical textile-finishing process has been limited. Instead, the research was focused on using binders to physically attach CD.

To chemically react a CD derivative with cellulose in an aqueous medium, CD was first reacted with NMA using an acid catalyst to obtain a vinyl monomer that can be grafted onto cellulose. NMA (CH_2═$CHCONHCH_2OH$) was selected since it is a versatile monomer which has a vinyl group capable of undergoing addition polymerization and a *N*-methylol group capable of undergoing condensation reactions, depending on the reaction conditions.

Synthesis of CD–NMA

The catalytic effects of hydrochloric acid, a mineral acid, formic acid, an organic acid, and ammonium dihydrogen phosphate ($NH_4H_2PO_4$), a salt, were compared by reacting 15 g of CD at an NMA/CD mol ratio of 10 at 80°C with the catalyst concentration fixed at 1%. Double-bond contents of the reaction products at different reaction times are shown in Figure 1. When hydrochloric acid was used as catalyst, the product at 5 min showed the highest double-bond content, which decreased slightly thereafter. However, when formic acid or ammonium dihydrogen phosphate was used, the double-bond content increased gradually with the reaction time up to 30 min, then leveled off. The double-bond content was lowest when ammonium dihydrogen phosphate was used.

The different behavior is attributed to the variation of pH with the type of catalyst used. The pH of 1% aqueous solutions of hydrochloric acid, formic acid, and ammonium dihydrogen phosphate were 1.51, 2.56, and 4.80, respectively. The reaction medium to which hydrochloric acid had been added had the lowest pH, and it appears that at a high pH the reaction does not occur as fast as or as extensively as at a lower pH. As can be seen in the following reaction, a carbonium ion is formed when acid is present and it is this carbonium ion that reacts with the hydroxy group of CD to form CD–NMA. Thus, the reaction occurs much slower at a higher pH:

$$CH_2{=}CHCONHCH_2OH + H^+ \rightleftharpoons CH_2{=}CHCONHC^+H_2 + H_2O$$

$$CH_2{=}CHCONHC^+H_2 + HO{-}CD \rightleftharpoons CH_2{=}CHCONHCH_2O{-}CD + H^+$$

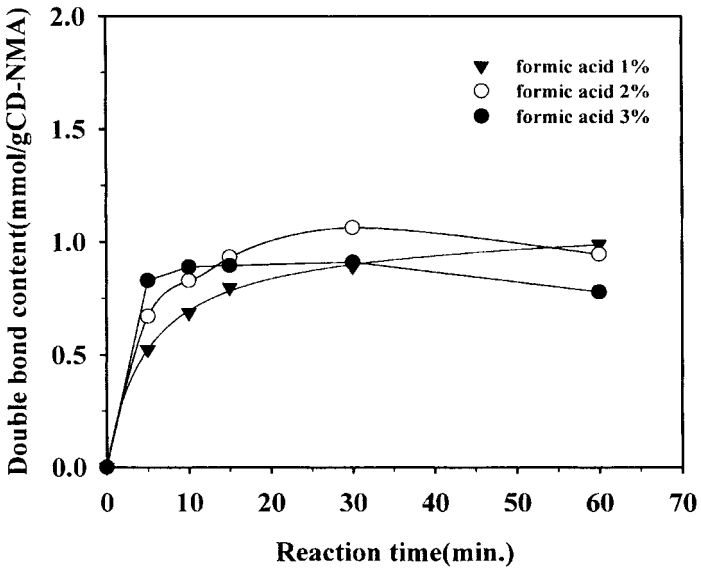

Figure 2 Changes in the double-bond content with reaction time in 1, 2, and 3% formic acid. Reaction conditions: CD, 15 g; CD : NMA, 1 : 10; water, 50 mL; temperature, 80°C.

Figure 2 shows the change in the double-bond content with the reaction time and the concentration of formic acid used as a catalyst. At higher catalyst concentrations, the double-bond content was initially higher but decreased slightly at longer reaction times, while at a lower catalyst concentration, it increased slowly. This behavior is similar to that seen in Figure 1. It appears that the reaction occurs faster at a lower pH, but at a lower pH, hydrolysis of CD–NMA also occurs to decrease the double-bond concentration slightly.

The effect of the reaction temperature can be seen in Figure 3. The optimum reaction temperature was 80°C when 2% of formic acid was used as a catalyst.

Figure 4 shows the double-bond contents of products obtained by reacting 20 g of CD at varying NMA/CD mol ratios at 80°C for 30 min with the concentration of the formic acid catalyst fixed at 2%. The double-bond content increases with the mol ratio of NMA/CD, and at the mol ratio of 30, the double-bond content is about 2.5 mmol/g CD–NMA, which corresponds to three molecules of NMA per CD molecule.

The absence of unreacted NMA in the acetone-washed reaction product was confirmed by the absence of the NMA peak at the elution time of 16.35 min in the HPLC analysis (Fig. 5). Therefore, the presence of CD in the cellulose fibers grafted with the CD–NMA monomer can be confirmed by infrared analysis of the attached NMA instead of the fluorescence analysis generally carried out to determine the presence of CD.

The amide I C═O stretching peak at 1670 cm^{-1}, the C═C vinyl stretching peak at 1628 cm^{-1}, and the amide II NH stretching peak at 1570 cm^{-1} can be seen in the infrared spectrum of the acetone-washed product in Figure 6, confirming that CD–NMA was synthesized.

The synthesis of CD–NMA is very simple compared with other CD vinyl monomers, such as

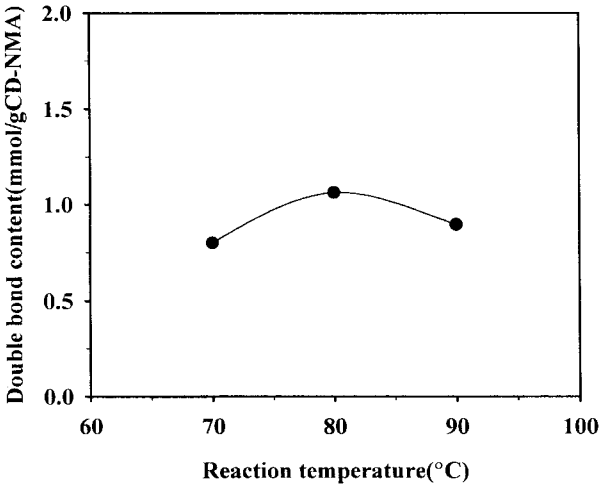

Figure 3 Effect of reaction temperature on double-bond content of CD–NMA. Reaction conditions: CD, 15 g; NMA, 1 : 10; water, 50 mL; time, 30 min; formic acid, 2%.

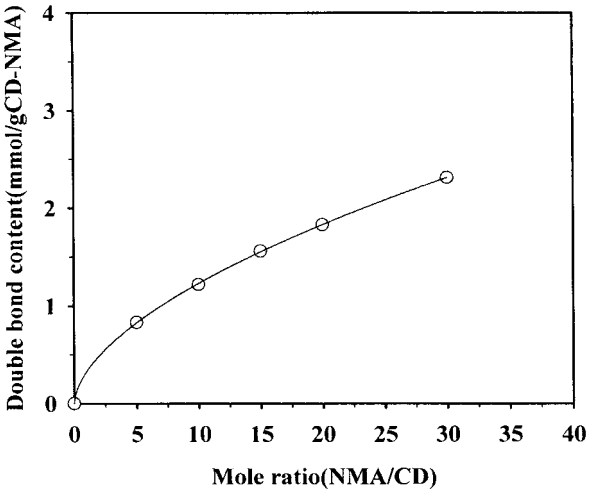

Figure 4 Dependence of double-bond content on the NMA/CD mol ratio. Reaction conditions: CD, 20 g; water, 50 mL; temperature, 80°C; time 30 min; formic acid, 2%.

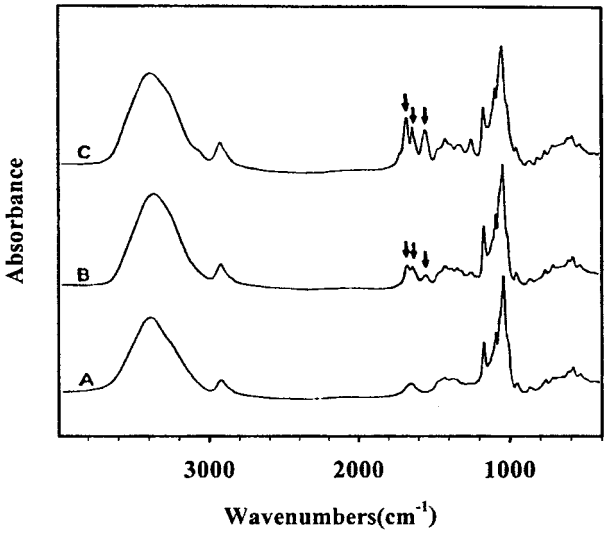

Figure 6 FTIR spectra of (A) CD, (B) CD–NMA (double-bond content, 0.9 mmol/g CD–NMA), and (C) CD–NMA (double-bond content, 1.85 mmol/g CD–NMA).

acryloyl CD or *N*-acryloyl-6-aminocaproyl CD synthesized by Harada et al.[7] in the preparation of water-soluble CD polymers. Furthermore, the feasibility of attaching three molecules of NMA to each CD molecule will allow a wide range of application in the synthesis of CD polymers and in the reactions with other polymers.

Acid Hydrolysis Behavior of CD–NMA

In the case of acrylamidomethylated cellulose, Kamel et al.[6] suggested that reduction in the double-bond content occurs in both alkaline and acidic media. Similarly, a reduction in the double-bond content may occur during grafting due to the acid employed with the CAN initiator. Therefore, to study the acid-catalyzed hydrolysis which may occur during graft copolymerization, 10 g of CD–NMA (double-bond content: 1.85 mmol/g CD–NMA) was dissolved in 50 mL of a 1% nitric acid solution and treated for different periods at 40 and 60°C, then precipitated with acetone. The double-bond contents decreased to an equilibrium value as the time of acid hydrolysis was extended; however, the initial decrease was more drastic when hydrolysis was carried out at 60°C compared with 40°C (Fig. 7). The double-bond content of the CD–NMA treated at 40°C decreased gradually to 0.5 mmol/g CD–NMA at 2 h, a value somewhat larger than that for the sample treated at 60°C. The double-bond content of the hydrolyzate in the residual solution did not change significantly with time, suggesting that the depletion of double bonds in CD–NMA occurs through the cleavage of the C—N bonds. In the infrared spectrum of the CD–NMA treated in 1% nitric acid at 60°C for 1 h (Fig. 8), decreases in the intensity of peaks at 1670, 1628, and 1570 cm^{-1} also substantiate the deduction that the cleavage of the C—N bond of CD–NMA causes the decrease in the double-bond content.

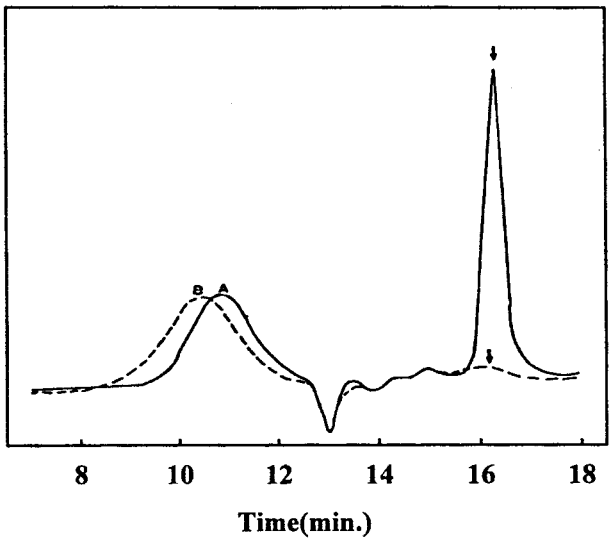

Figure 5 HPLC chromatograms of (A) mixture of CD and NMA and (B) reaction product (CD–NMA) after acetone washing.

The residual double-bond content of CD–NMA treated in 1% nitric acid for 40 min at 30, 40, 50, 60, and 70°C (Fig. 9) decreases with increase in

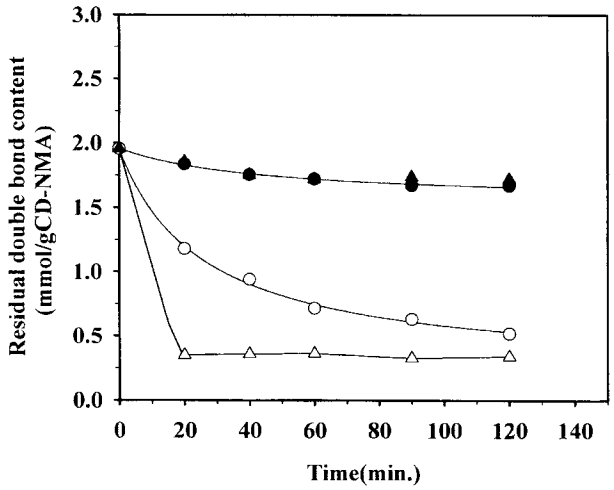

Figure 7 Changes in the residual double-bond contents of the (filled symbols) hydrolyzate and (open symbols) CD–NMA with the time of hydrolysis at (○, ●) 40 and (△, ▲) 60°C. Reaction conditions: CD–NMA, 10 g; 1% HNO_3, 50 mL.

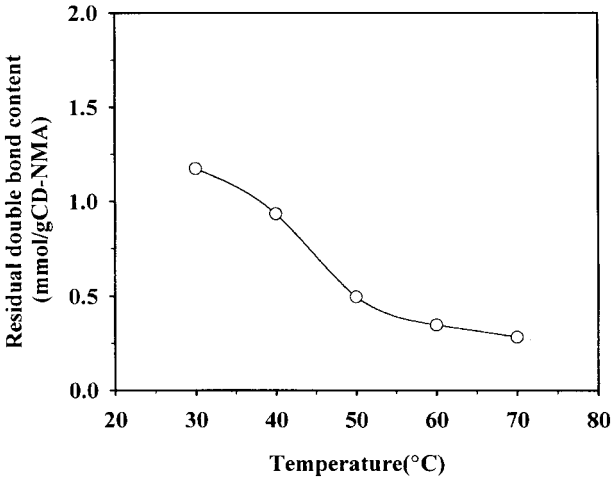

Figure 9 Effect of hydrolysis temperature on the residual double-bond content of the CD–NMA. Reaction conditions: CD–NMA (1.85 mmol/g CD–NMA), 10 g; water, 50 mL; HNO_3, 1%; time, 40 min.

the treatment temperature. The decrease was drastic at 40–50°C, and at 70°C, the residual double-bond content was 0.25 mmol/g CD–NMA. Therefore, if the efficiency of the ceric ion initiator does not change significantly with temperature, a grafting temperature of 40°C where hydrolysis does not occur extensively should be more advantageous for higher grafting efficiency.

The effect of the concentration of acid on the residual double-bond content after 40-min treatment in nitric acid at 40 or 60°C (Fig. 10) is not significant except at very low concentrations, while the effect of the treatment temperature was significant in all the acid concentrations studied, that is, the reaction temperature has a more significant effect on the decrease of double bonds compared with the concentration of the acid.

The results suggest that the effect of the reaction temperature is greater than is the concentration of acid in the acid hydrolysis of CD–NMA. Thus, lower temperatures and nitric acid concentrations of the CAN initiator solution should be used in the grafting of CD–NMA onto cellulose to obtain high grafting efficiency.

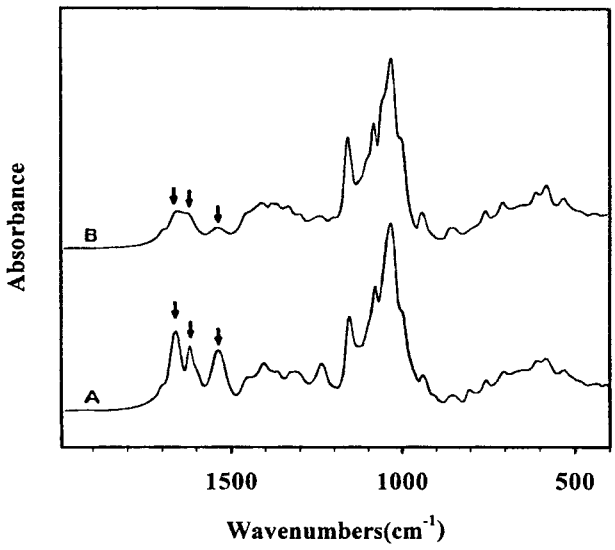

Figure 8 FTIR spectra of CD–NMA: (A) before acid hydrolysis; (B) after acid hydrolysis (60 C, 1 h).

Grafting of CD–NMA onto Cellulose

Although extensive research on the graft copolymerization of cellulose and cellulose derivatives has been reported and the mechanisms well established, the grafting of CD–NMA has not been reported. Graft copolymerization may be carried out by various methods, but radical polymerization initiated by the ceric redox initiator was selected as it can be carried out at lower temperatures with reduced homopolymer formations and is relatively simple. After grafting of cotton fibers with CD–NMA (double-bond content: 1.85 mmol/g CD–NMA) at 40 and 60°C, the samples were thoroughly washed to completely remove homopolymers and unreacted CD–NMA. We obtained grafted cotton fibers of 34 and 65% yields, respec-

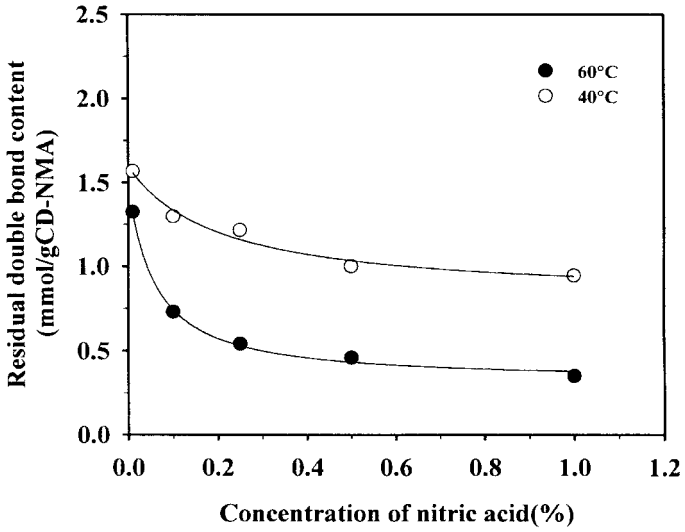

Figure 10 Effect of acid concentration on the residual double-bond content of CD–NMA. Reaction conditions: CD–NMA (1.85 mmol/g CD–NMA), 10 g; water, 50 mL; time, 40 min.

tively, and infrared analysis was carried out to verify the presence of grafted CD–NMA. Considering the structure and the molecular weight of CD–NMA, it is believed that the grafting occurred mainly on the surface of the cellulose.

In the infrared spectra of cellulose and CD in Figure 11, CD exhibits characteristic peaks at 944, 853, and 756 cm^{-1}, which are absent in cellulose. The peaks at 853 and 756 cm^{-1} are the CH deformation and ring-breathing modes of α-polysaccharides, respectively.[8]

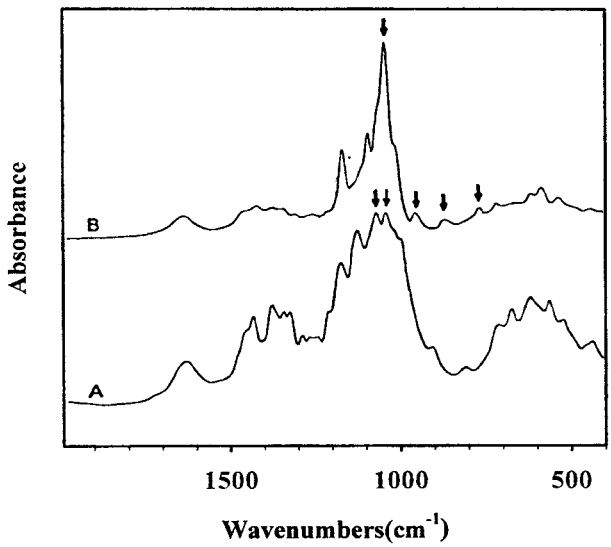

Figure 11 FTIR spectra of (A) cellulose and (B) β-CD.

The reaction of CD–NMA with cellulose can also be confirmed by the presence of amide II band at 1570 cm^{-1} in the infrared spectra of the grafted fiber. The infrared spectrum of the grafted cotton fiber in Figure 12 exhibits peaks at both 1570 and 756 cm^{-1}, confirming the reaction of CD–NMA with cellulose fibers.

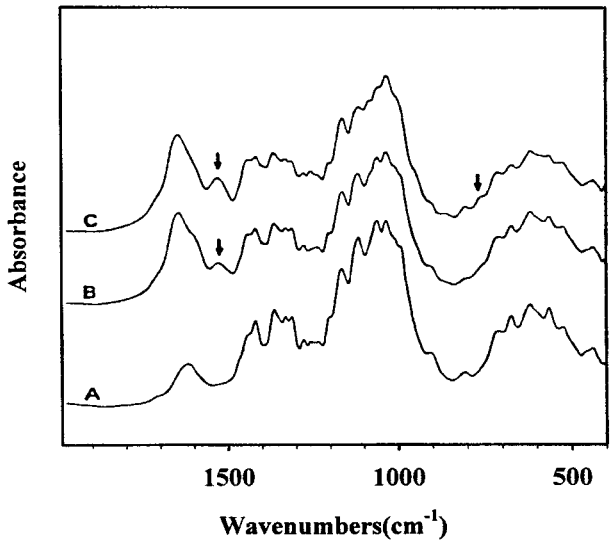

Figure 12 FTIR spectra of (A) cotton fiber, (B) grafted fiber (yield 34%), and (C) grafted fiber (yield 65%).

CONCLUSIONS

β-Cyclodextrin (CD) can be chemically attached to cellulose by synthesizing acrylamidomethyl CD (CD–NMA) containing a double bond and grafting the CD–NMA onto cellulose fibers.

1. The CD–NMA monomer can be synthesized by reacting NMA with CD using an acid catalyst. When hydrochloric acid or formic acid is used as the catalyst at 80°C, the respective reaction times of 15 and 30 min are sufficient.
2. The double-bond content of the CD–NMA product increased proportionally with the NMA/CD mol ratio and the highest content obtained, 2.54 mmol/g CD–NMA, corresponds to approximately three molecules of NMA per CD molecule. The CD–NMA undergoes hydrolysis in acid solutions, and the temperature had a more significant effect on the hydrolysis compared with the concentration of acid within the range of this study.
3. The formation of chemically attached CD through grafting onto cellulose fibers was confirmed by the infrared analysis of the grafted products from which homopolymers and unreacted monomers had been removed.

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